



# Spectroscopic identification of a novel catalytic reaction of potassium and atomic hydrogen and the hydride ion product

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## Abstract

From a solution of a Schrödinger-type wave equation with a nonradiative boundary condition based on Maxwell's equations, Mills predicts that atomic hydrogen may undergo a catalytic reaction with certain atomized elements and ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV. The reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen with the release of energy. One such atomic catalytic system involves potassium atoms. The first, second, and third ionization energies of potassium are 4.34066, 31.63, and 45.806 eV, respectively. The triple ionization ( $t=3$ ) reaction of  $K-K^{3+}$ , then, has a net enthalpy of reaction of 81.7766 eV, which is equivalent to  $3 \times 27.2$  eV. Intense extreme ultraviolet (EUV) emission was observed from incandescently heated atomic hydrogen and the atomized potassium catalyst that generated an anomalous plasma at low temperatures (e.g.  $\approx 10^4$  K) and an extraordinary low field strength of about 1-2 V/cm. No emission was observed with potassium or hydrogen alone or when sodium replaced potassium with hydrogen. Emission was observed from  $K^{3+}$  confirmed the resonant nonradiative energy transfer of  $3 \times 27.2$  eV from atomic hydrogen to atomic potassium. The catalysis product, a lower-energy hydrogen atom, was predicted to be a highly reactive intermediate which further reacts to form a novel hydride ion. The predicted hydride ion of hydrogen catalysis by atomic potassium is the hydride ion  $H^-$  (1/4). This ion was observed spectroscopically at 11.6 nm corresponding to its predicted binding energy of 11.2 eV. © 2001 Published by Elsevier Science Ltd. on behalf of the International Association for Hydrogen Energy.

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## 1. Introduction

Based on the solution of a Schrödinger-type wave equation with a nonradiative boundary condition based on Maxwell's equations, Mills [1-38] predicts that atomic hydrogen may undergo a catalytic reaction with certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV. For example, cesium atoms ionize at an integer multiple of the potential energy of atomic hydrogen,  $m \times 27.2$  eV. The enthalpy of ionization of  $Cs-Cs^{2+}$  has a net enthalpy of reaction of 27.05135 eV,

which is equivalent to  $m=1$  [39]. The reaction  $Ar^+-Ar^{2+}$  has a net enthalpy of reaction of 27.63 eV, which is equivalent to  $m=1$  [39]. In each case, the reaction involves a nonradiative energy transfer to form a hydrogen atom that is lower in energy than unreacted atomic hydrogen. The product hydrogen atom has an energy state that corresponds to a fractional principal quantum number. Recent analysis of mobility and spectroscopy data of individual electrons in liquid helium show direct experimental confirmation that electrons may have fractional principal quantum energy levels [35]. The lower-energy hydrogen atom is a highly reactive intermediate which further reacts to form a novel hydride ion. Emission was observed previously from a continuum state of  $Cs^{2+}$  and  $Ar^{2+}$  at 53.3 and 45.6 nm, respectively [5]. The single emission feature with the absence of the other corresponding Rydberg series of lines from these species

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confirmed the resonant nonradiative energy transfer of 27.2 eV from atomic hydrogen to atomic cesium or  $\text{Ar}^+$ . The catalysis product, a lower-energy hydrogen atom, was predicted to be a highly reactive intermediate which further reacts to form a novel hydride ion. The predicted hydride ion of hydrogen catalysis by either cesium atom or  $\text{Ar}^+$  catalyst is the hydride ion  $\text{H}^-(1/2)$ . This ion was observed spectroscopically at 407 nm corresponding to its predicted binding energy of 3.05 eV. The catalytic reactions with the formation of the hydride ions are given in Appendix A.

Additional prior studies that support the possibility of a novel reaction of atomic hydrogen which produces an anomalous discharge and produces novel hydride compounds include extreme ultraviolet (EUV) spectroscopy [5,7–20], plasma formation [5–20], power generation [6–8,13,36], and analysis of chemical compounds [16,18–34]. Typically, the emission of extreme ultraviolet light from hydrogen gas is achieved via a discharge at high voltage, a high power inductively coupled plasma, or a plasma created and heated to extreme temperatures by RF coupling (e.g.  $> 10^6$  K) with confinement provided by a toroidal magnetic field. Observation of intense extreme ultraviolet (EUV) emission at low temperatures (e.g.  $\approx 10^3$  K) from atomic hydrogen and certain atomized elements or certain gaseous ions has been reported previously [5,7–20]. The only pure elements that were observed to emit EUV were those predicted [1–38] wherein the ionization of  $i$  electrons from an atom or ion to a continuum energy level is such that the sum of the ionization energies of the  $i$  electrons is approximately  $m \times 27.2$  eV where  $i$  and  $m$  are each an integer.

The observed EUV emission could not be explained by conventional chemistry; rather it must have been due to a novel chemical reaction between catalyst and atomic hydrogen. The catalysis of hydrogen involves the nonradiative transfer of energy from atomic hydrogen to a catalyst which may then release the transferred energy by radiative and nonradiative mechanisms. As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (A.1) and (A.2) of Appendix A.

The energy released during catalysis may undergo internal conversion and ionize or excite molecular and atomic hydrogen resulting in hydrogen emission which includes well characterized ultraviolet lines such as the Lyman series. Lyman series emission, emission due to the catalyst mechanism, and emission of the hydride ion product were measured by EUV spectroscopy. The catalytic reactions and binding energies of the product hydride ions are given in Appendix A.

Potassium, cesium, and strontium atoms and  $\text{Rb}^+$  ion ionize at integer multiples of the potential energy of atomic hydrogen. In prior studies [5,7–20] and in the current experiments, these catalysts caused intense extreme ultraviolet (EUV) emission from incandescently heated atomic

hydrogen and the atomized catalyst that generated a plasma at low temperatures (e.g.  $\approx 10^3$  K). Whereas, the chemically similar noncatalyst atoms, sodium, magnesium and barium, do not ionize at integer multiples of the potential energy of atomic hydrogen, did not generate a plasma, and caused no emission. In the case of atomic potassium catalyst, the first, second, and third ionization energies are 4.34066, 31.63, 45.806 eV, respectively. The triple ionization ( $i=3$ ) reaction of  $\text{K}-\text{K}^{3+}$ , then, has a net enthalpy of reaction of 81.7766 eV, which is equivalent to  $3 \times 27.2$  eV. Emission was observed from  $\text{K}^{3+}$  that confirmed the resonant nonradiative energy transfer of  $3 \times 27.2$  eV from atomic hydrogen to atomic potassium. The predicted hydride ion of hydrogen catalysis by atomic potassium is the hydride ion  $\text{H}^-(1/4)$ . This ion was observed spectroscopically at 110 nm corresponding to its predicted binding energy of 11.2 eV.

## 2. Experimental

### 2.1. EUV spectroscopy

Due to the extremely short wavelength of this radiation, "transparent" optics do not exist. Therefore, a windowless arrangement was used wherein the source was connected to the same vacuum vessel as the grating and detectors of the EUV spectrometer. Windowless EUV spectroscopy was performed with an extreme ultraviolet spectrometer that was mated with the cell. Differential pumping permitted a high pressure in the cell as compared to that in the spectrometer. This was achieved by pumping on the cell outlet and pumping on the grating side of the collimator that served as a pin-hole inlet to the optics. The cell was operated under hydrogen flow conditions while maintaining a constant hydrogen pressure in the cell with a mass flow controller.

The experimental set up shown in Fig. 1 comprised a quartz cell which was 500 mm in length and 50 mm in diameter. Three ports for gas inlet, outlet, and photon detection were on the cap of the cell. The cell pump was a

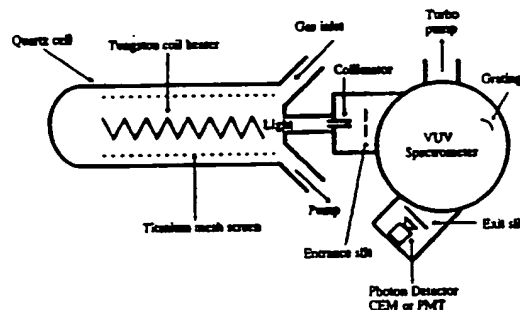


Fig. 1. The experimental set up comprising a gas cell light source and an EUV spectrometer which was differentially pumped.

mechanical pump. The spectrometer was continuously evacuated to  $10^{-4}$ – $10^{-6}$  Torr by a turbomolecular pump with the pressure read by a cold cathode pressure gauge. The EUV spectrometer was connected to the cell light source with a 1.5 mm  $\times$  5 mm collimator which provided a light path to the slits of the EUV spectrometer. The collimator also served as a flow constrictor of gas from the cell. Valves were between the cell and the mechanical pump, the cell and the monochromator, and the monochromator and its turbo pump.

A tungsten filament (0.508 mm in diameter and 800 cm in length, total resistance  $\sim 2.5 \Omega$ ) and a titanium cylindrical screen (300 mm long and 40 mm in diameter) that performed as a hydrogen dissociator were inside the quartz cell. A new dissociator was used for each experiment. The filament was coiled on a grooved ceramic support to maintain its shape when heated. The return lead ran through the middle of the ceramic support. The filament leads were covered by an alumina sheath. The titanium screen was electrically floated. The power was applied to the filament by a power supply (Sorensen 80-13) which was controlled by a constant power controller. For the catalysts, the cell was operated with a maximum of 300 W of input power which corresponded to a cell wall temperature of about 700 °C. The temperature of the tungsten filament was estimated to be about 1500 °C. In the case of the noncatalysts, the cell power was increased to the maximum of 500 W. The gas was ultra-high purity hydrogen. The gas pressure inside the cell was maintained at about 300 mTorr with a hydrogen flow rate of 5.5 sccm controlled by a 0–20 sccm range mass flow controller (MKS 1179A21CS1BB) with a readout (MKS type 246). The entire quartz cell was enclosed inside an insulation package (Zircar AL-30). Several K-type thermocouples were placed in the insulation to measure key temperatures of the cell and insulation. The thermocouples were read with a multichannel computer data acquisition system.

In the present study, the light emission phenomena was studied for (1) hydrogen, argon, neon, and helium alone, (2) sodium, rubidium, magnesium, strontium, and barium metals, and (3)  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Cs}_2\text{CO}_3$ . The inorganic test materials were coated on a titanium screen dissociator by the method of wet impregnation. The screen was coated by dipping it in a 0.6 M  $\text{Na}_2\text{CO}_3$ /10%  $\text{H}_2\text{O}_2$ , 0.6 M  $\text{K}_2\text{CO}_3$ /10%  $\text{H}_2\text{O}_2$ , or 0.6 M  $\text{Cs}_2\text{CO}_3$ /10%  $\text{H}_2\text{O}_2$  solution, and the crystalline material was dried on the surface by heating for 12 h in a drying oven at 130 °C. A new dissociator was used for each experiment. The metals were placed in the bottom of the cell and volatilized by the filament heater.

The light emission was introduced to an EUV spectrometer for spectral measurement. The spectrometer was a McPherson 0.2 m monochromator (Model 302, Seya-Namioka type) equipped with a 1200 lines/mm holographic grating with a platinum coating. The wavelength region covered by the monochromator was 30–560 nm. The vacuum inside the monochromator was maintained below  $5 \times 10^{-4}$  Torr by a turbo pump.

The EUV spectrum (40–160 nm) of the cell emission was recorded with a channel electron multiplier (CEM). The wavelength resolution was about 1 nm (FWHM) with an entrance and exit slit width of 300  $\mu\text{m}$ .

The EUV/UV/VIS spectrum (40–560 nm) of the cell emission with hydrogen alone was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. The PMT (Model R1527P, Hamamatsu) used has a spectral response in the range of 185–680 nm with a peak efficiency at about 400 nm. The scan interval was 0.4 nm. The inlet and outlet slit were 500  $\mu\text{m}$  with a corresponding wavelength resolution of 2 nm.

## 2.2. Standard potassium emission spectrum

The standard extreme ultraviolet emission spectrum of potassium was obtained with a gas discharge cell comprised of a five-way stainless steel cross that served as the anode with a hollow stainless steel cathode that was coated with  $\text{K}_2\text{CO}_3$  by the same procedure used to coat the titanium dissociator. The five-way cross was pressurized with 1 Torr of hydrogen to initiate the discharge. The hydrogen was then evacuated so that only potassium lines were observed. The DC voltage at the time the EUV spectrum was recorded was 300 V.

## 3. Results

### 3.1. EUV spectroscopy

The intensity of the Lyman  $\alpha$  emission as a function of time from the gas cell at a cell temperature of 700 °C comprising a tungsten filament, a titanium dissociator, and 300 mTorr hydrogen with a flow rate of 5.5 sccm was tested for several controls and catalysts. The cell was run with hydrogen but without any test material present to establish the baseline of the spectrometer. The intensity of the Lyman  $\alpha$  emission as a function of time was measured for 3 h, and no emission was observed. The corresponding UV/VIS spectrum (40–560 nm) is shown in Fig. 2. The spectrum was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. No emission was observed except for the blackbody filament radiation at the longer wavelengths. No emission was also observed for the pure elements alone or when argon, neon, or helium replaced hydrogen. Sodium, magnesium, or barium metal was vaporized by filament heating. Sodium metal was also vaporized from  $\text{Na}_2\text{CO}_3$  as the source. No emission was observed in any case. The maximum filament power was greater than 500 W. A metal coating formed in the cap of the cell over the course of the experiment in all cases.

The intensity of the Lyman  $\alpha$  emission as a function of time with each of vaporized cesium from  $\text{Cs}_2\text{CO}_3$ , potassium from  $\text{K}_2\text{CO}_3$ ,  $\text{Rb}^+$  from rubidium metal, and strontium from strontium metal was recorded. In all cases, strong

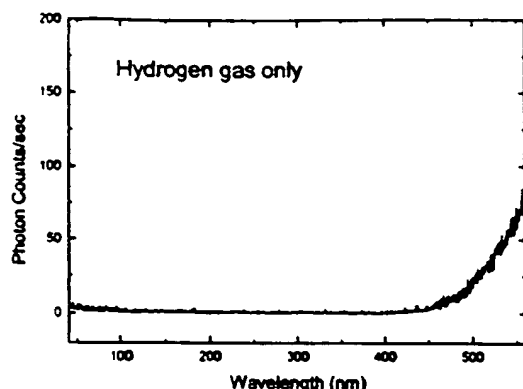


Fig. 2. The UV/VIS spectrum (40–560 nm) of the cell emission from the gas cell at a cell temperature of 700°C comprising a tungsten filament, a titanium dissociator, and 300 mTorr hydrogen that was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator with an entrance and exit slit width of 500 μm. No emission was observed except for the blackbody filament radiation at the longer wavelengths.

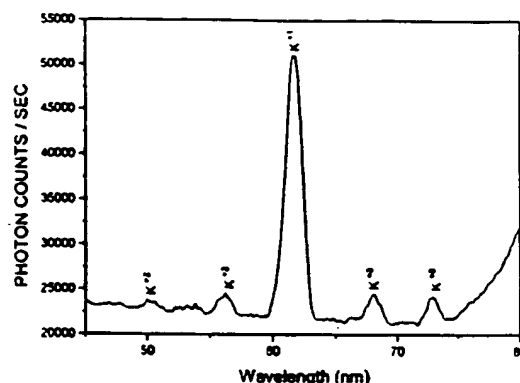


Fig. 4. The EUV spectrum (45–80 nm) of the cell emission recorded at about the point of the maximum Lyman α emission from the gas cell at a cell temperature of 700°C comprising a tungsten filament, a titanium dissociator, 300 mTorr hydrogen, and vaporized potassium from  $K_2CO_3$  that was recorded with a CEM. Line emission corresponding to  $K^+$  was observed at 65–67 and 74–76 nm.

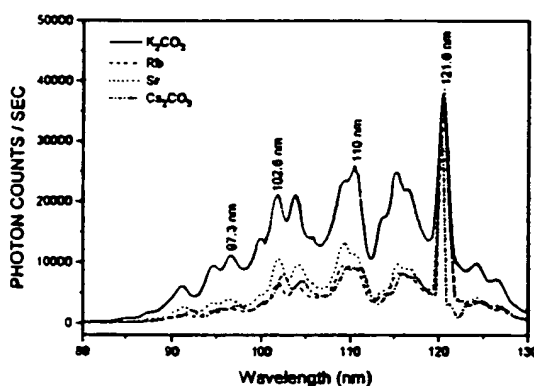


Fig. 3. The EUV spectrum (80–130 nm) of the cell emission recorded at about the point of the maximum Lyman α emission from the gas cell at a cell temperature of 700°C comprising a tungsten filament, a titanium dissociator, 300 mTorr hydrogen, and each of vaporized cesium from  $Cs_2CO_3$ , rubidium from Rb, and strontium from Sr that was recorded with a CEM. The ratio of the intensities of the hydrogen peaks  $B^1\Sigma^+ \rightarrow X^1\Sigma^+$  for  $n = 1-6$  and  $1-5$  at 109.989 and 108.946 nm, respectively is 0.68.

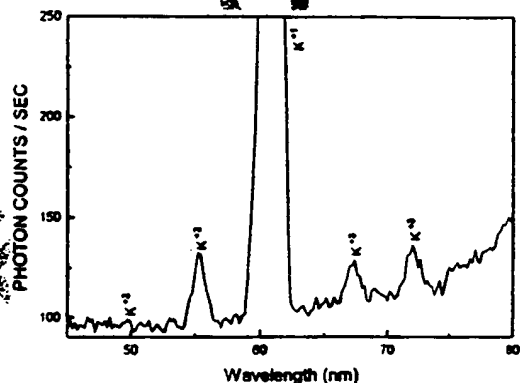


Fig. 5. The EUV spectrum (45–80 nm) of the cell emission recorded at about the point of the maximum Lyman α emission from a repeat gas cell at a cell temperature of 700°C comprising a tungsten filament, a titanium dissociator, 300 mTorr hydrogen, and vaporized potassium from  $K_2CO_3$  that was recorded with a CEM. Line emission corresponding to  $K^{3+}$  was observed at 65–67 and 74–76 nm.

of a metal coating in the cap of the cell over the course of the experiment.

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- 1 EUV emission was observed from vaporized catalyst with hydrogen. The superposition of the EUV spectra (80–
- 3 130 nm) of the cell emission recorded at about the point of the maximum Lyman α emission for each of the catalysts is shown in Fig. 3. In each case, no emission was observed in the absence of hydrogen, and no emission occurred until the catalyst was vaporized as indicated by the appearance

### 3.2. EUV emission of potassium catalyst

The EUV spectrum (45–80 nm) of the emission of the potassium–hydrogen gas cell and a replication experiment are shown in Figs. 4 and 5. Line emission corresponding to  $K^{3+}$  was observed at 65–67 and 74–76 nm.  $K^{2+}$  was observed at 51 and 55 nm, and  $K^+$  was observed at 62 nm.

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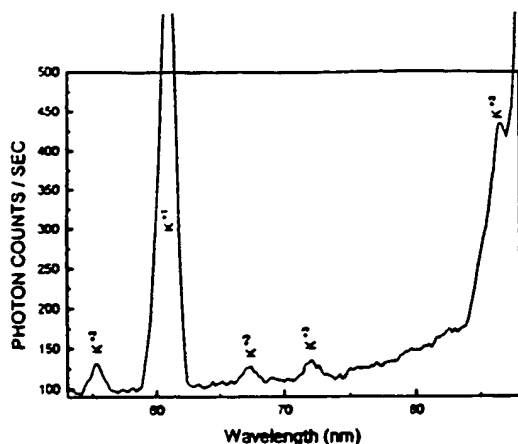


Fig. 6. The EUV spectrum (53–89 nm) of the cell emission recorded at about the point of the maximum Lyman  $\alpha$  emission from a repeat gas cell at a cell temperature of 700°C comprising a tungsten filament, a titanium dissociator, 300 mTorr hydrogen, and vaporized potassium from  $K_2CO_3$  that was recorded with a CEM. A large  $K^{3+}$  peak was observed at 89.2 nm.

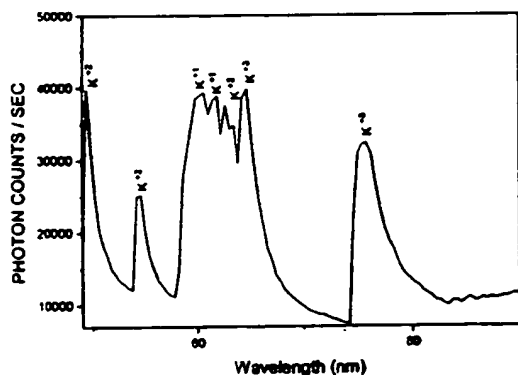


Fig. 7. The EUV spectrum (50–90 nm) recorded from a standard potassium plasma excited by a discharge cell which comprised a five-way stainless steel cross that served as the anode with a hollow stainless steel cathode. The assignments of the  $K^{3+}$ ,  $K^{2+}$ , and  $K^{1+}$  lines were confirmed by the standard potassium plasma spectrum.

- 1 A large  $K^{3+}$  peak shown in Fig. 6 was also observed at 89.2 nm. The assignments of the  $K^{3+}$ ,  $K^{2+}$ , and  $K^{1+}$  lines
- 3 were confirmed by the standard potassium plasma spectrum shown in Fig. 7 and NIST tables [40,41].

### 5 3.3. 110 nm emission with potassium catalyst

- 7 The EUV spectrum (80–130 nm) of the cell emission from the potassium gas cell and a replication experiment are shown in Figs. 8 and 9. The EUV spectrum (80–130 nm)

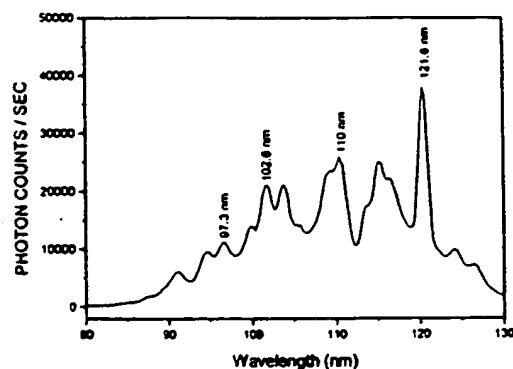


Fig. 8. The EUV spectrum (80–130 nm) of the cell emission recorded at about the point of the maximum Lyman  $\alpha$  emission from the gas cell at a cell temperature of 700°C comprising a tungsten filament, a titanium dissociator, 300 mTorr hydrogen, and vaporized potassium from  $K_2CO_3$  that was recorded with a CEM. The ratio of the peak at 110 nm versus the hydrogen peak at 108.946 nm is 1.19. Whereas, the peaks at these wavelengths in the controls shown in Fig. 3 are 0.883. The increase in intensity at 110 nm compared to hydrogen emission alone was assigned to a contribution from  $H^-(1/4)$ .

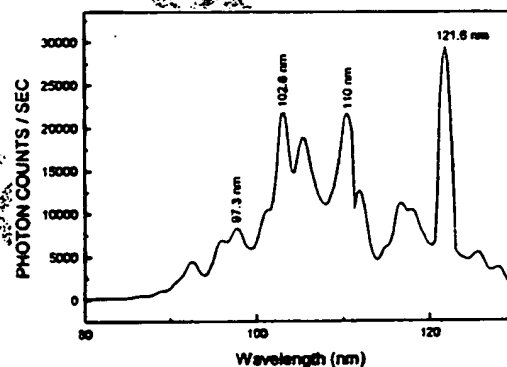


Fig. 9. The EUV spectrum (80–130 nm) of the cell emission recorded at about the point of the maximum Lyman  $\alpha$  emission from a repeat gas cell at a cell temperature of 700°C comprising a tungsten filament, a titanium dissociator, 300 mTorr hydrogen, and vaporized potassium from  $K_2CO_3$  that was recorded with a CEM. The ratio of the peak at 110 nm versus the hydrogen peak at 108.946 nm is 1.61. Whereas, the peaks at these wavelengths in the controls shown in Fig. 3 is 0.883. The increase in intensity at 110 nm compared to hydrogen emission alone was assigned to a contribution from  $H^-(1/4)$ .

of the cell emission from the cesium, potassium, rubidium, and strontium gas cells are superimposed in Fig. 3. Only potassium is predicted to form the hydride  $H^-(1/4)$  with emission at 110 nm as shown in Appendix A and Table 1. Molecular hydrogen has peaks in this region as shown in Fig. 3 for catalysts which form a plasma in hydrogen but

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Table 1

The ionization energy of the hydrido hydride ion  $H^-(n=1/p)$  as a function of  $p$

Hydride ion	Catalyst	$r_1$ ( $a_0$ ) <sup>a</sup>	Calculated ionization energy <sup>b</sup> (eV)	Calculated wavelength (nm)
$H^-(n=1)$		1.8660	0.754	1645
$H^-(n=1/2)$	$Rb^+, Cs$	0.9330	3.047	407
$H^-(n=1/3)$		0.6220	6.610	188
$H^-(n=1/4)$	K	0.4665	11.23	110
$H^-(n=1/5)$		0.3732	16.70	74.2
$H^-(n=1/6)$		0.3110	22.81	54.4
$H^-(n=1/7)$		0.2666	29.34	42.3
$H^-(n=1/8)$	Sr	0.2333	36.08	34.4
$H^-(n=1/9)$		0.2073	42.83	28.9
$H^-(n=1/10)$		0.1866	49.37	25.1
$H^-(n=1/11)$		0.1696	55.49	22.34
$H^-(n=1/12)$		0.1555	60.98	20.33
$H^-(n=1/13)$		0.1435	65.62	18.89
$H^-(n=1/14)$		0.1333	69.21	17.91
$H^-(n=1/15)$		0.1244	71.53	17.33
$H^-(n=1/16)$		0.1166	72.38	17.13
$H^-(n=1/17)$		0.1098	71.54	17.33
$H^-(n=1/18)$		0.1037	68.80	18.02
$H^-(n=1/19)$		0.0982	63.95	19.39
$H^-(n=1/20)$		0.0933	56.78	21.83
$H^-(n=1/21)$		0.0889	47.08	26.33
$H^-(n=1/22)$		0.0848	34.63	35.80
$H^-(n=1/23)$		0.0811	19.22	64.49
$H^-(n=1/24)$		0.0778	0.6535	1897
$H^-(n=1/25)$			Not stable	

<sup>a</sup>From Eq. (A.15).

<sup>b</sup>From Eq. (A.16).

- 1 are predicted to form a hydride different from  $H^-(1/4)$ .  
 2 The hydrogen peaks in the region of 110 nm are due to the  
 3 transition  $B^1\Sigma_g^+ \rightarrow X^1\Sigma_g^+$ . A peak at 109.989 nm is due  
 4 to  $v=1-6$ , and a peak at 108.946 nm is due to  $v=1-2$ . The  
 5 experimental emission intensity ratio from Fig. 8 is  

$$\frac{\text{Intensity}(109.989)}{\text{Intensity}(108.946)} = \frac{13,701 \text{ photon counts/s}}{15,506 \text{ photon counts/s}} = 0.883, \quad (1)$$

- 6 whereas the ratio of the peak at 110 nm versus the peak at  
 7 108.946 nm with potassium catalyst and hydrogen shown in  
 8 Fig. 8 is

$$\frac{\text{Intensity}(110)}{\text{Intensity}(108.946)} = \frac{27,850 \text{ photon counts/s}}{22,280 \text{ photon counts/s}} = 1.19. \quad (2)$$

- 9 The ratio of the peak at 110 nm versus the peak at  
 10 108.946 nm with potassium catalyst and hydrogen shown  
 11 in Fig. 9 is

$$\frac{\text{Intensity}(110)}{\text{Intensity}(108.946)} = \frac{21,723 \text{ photon counts/s}}{13,462 \text{ photon counts/s}} = 1.61. \quad (3)$$

- 12 The 110 nm peak is twice that of the control molecular hy-  
 13 drogen peak. This peak dominated the molecular hydrogen

peak at 108.946 nm such that the counts due to each peak  
 were determined by expanding the scale and deconvolving  
 the superimposed peaks. Potassium does not have emission  
 lines in the region of 110 nm. Thus, from the comparison,  
 a novel continuum feature is observed at 110 nm which  
 was not due to hydrogen or potassium emission. The novel  
 110 nm continuum peak was observed only with potassium  
 and atomic hydrogen present over an extended reaction time.  
 As shown in Figs. 8 and 3, the Lyman  $\beta$  and Lyman  $\delta$  lines  
 of the potassium gas cell at 102.6 and 97.3 nm, respectively,  
 have a greater intensity relative to Lyman  $\alpha$  line at 121.6 nm  
 than the other catalysts which indicates a high plasma tem-  
 perature. These results are consistent with the formation of  
 $H^-(1/4)$  from the catalysis of atomic hydrogen by K(m).

#### 4. Discussion

A plasma that emitted intense EUV formed at low tem-  
 peratures (e.g.  $\approx 10^3$  K) from atomic hydrogen and each of  
 $Rb^+$ , cesium, potassium, and strontium catalyst which was  
 vaporized by heating. No possible chemical reactions of the  
 tungsten filament, the dissociator, the vaporized test mate-  
 rial, and 300 mTorr hydrogen at a cell temperature of 700°C  
 could be found which accounted for the hydrogen Lyman  $\alpha$   
 line emission. In fact, no known chemical reaction releases  
 enough energy to excite Lyman  $\alpha$  emission from hydrogen.  
 The emission was not observed with catalyst or hydrogen  
 alone. Intense emission was observed for catalyst with hy-  
 drogen gas, but no emission was observed when sodium,  
 magnesium, or barium replaced a catalyst with hydrogen.  
 This result indicates that the emission was due to a reaction  
 of the catalyst with hydrogen.

The only pure elements that were observed to emit EUV  
 were those wherein the ionization of  $l$  electrons from an  
 atom or ion to a continuum energy level is such that the sum  
 of the ionization energies of the  $l$  electrons is approximately  
 $m \times 27.2$  eV where  $l$  and  $m$  are each an integer. Rubidium  
 ions and potassium, cesium, and strontium atoms ionize at an  
 integer multiple of the potential energy of atomic hydrogen,  
 $m \times 27.2$  eV. The triple ionization ( $l=3$ ) reaction of  
 $K-K^{3+}$  has a net enthalpy of reaction of 81.7766 eV, which  
 is equivalent to  $m=3$ . The reaction  $Rb^+ \rightarrow Rb^{2+}$  has a net  
 enthalpy of reaction of 27.28 eV, which is equivalent to  
 $m=1$ . The double ionization ( $l=2$ ) of  $Cs-Cs^{2+}$  has a net  
 enthalpy of reaction of 27.05135 eV, which is equivalent to  
 $m=1$  [39]. The ionization reaction of  $Sr-Sr^{2+}$ , ( $l=5$ ) has  
 a net enthalpy of reaction of 188.2 eV, which is equivalent  
 to  $m=7$ . In each case, the reaction involves a nonradiative  
 energy transfer to form a hydrogen atom that is lower in  
 energy than unreacted atomic hydrogen.

Characteristic emission was observed from  $K^{3+}$  which  
 confirmed the resonant nonradiative energy transfer of  
 $3 \times 27.2$  eV from atomic hydrogen to atomic potassium  
 (Eq. (A.5)). With a highly conductive plasma, the voltage of  
 the cell was about 20 V, and the field strength was about

1–2 V/cm which was too low to ionize potassium to  $K^{3+}$  which requires at least 81.7766 eV. The  $K^{3+}$  lines generated in the incandescently heated cell and due to the catalyst reaction of atomic hydrogen were confirmed by a high voltage discharge and NIST tables [40,41].

$K(m)$  is predicted to catalyze hydrogen to form  $H(\alpha_H/4)$  which reacts with an electron to form  $H^-(1/4)$ . The predicted  $H^-(1/4)$  hydride ion of hydrogen catalysis by potassium was observed spectroscopically at 110 nm corresponding to its predicted binding energy of 11.2 eV. The hydride reaction product formed over time.

The release of energy from hydrogen as evidenced by the EUV emission must result in a lower-energy state of hydrogen. The present study identified the formation of a novel hydride ion. The formation of novel compounds based on novel hydride ions would be a substantial evidence supporting catalysis of hydrogen as the mechanism of the observed EUV emission and further support the present spectroscopic identification of  $H^-(1/4)$ . Compounds containing novel hydride ions have been isolated as products of the reaction of atomic hydrogen with atoms and ions identified as catalysts in the present study and previously reported EUV studies [5,7–34,36]. The novel hydride compounds were identified analytically by techniques such as time of flight secondary ion mass spectroscopy, X-ray photoelectron spectroscopy, and  $^1H$  nuclear magnetic resonance spectroscopy. For example, the time of flight secondary ion mass spectroscopy showed a large hydride peak in the negative spectrum. The X-ray photoelectron spectrum showed large metal core level shifts due to binding with the hydride as well as novel hydride peaks. The  $^1H$  nuclear magnetic resonance spectrum showed significantly upfield shifted peaks which corresponded to and identified novel hydride ions.

The hydride ion  $H^-(1/4)$  has been reported previously [22]. KHI containing  $H^-(1/4)$  was synthesized by reaction of potassium metal, atomic hydrogen, and KI. The XPS spectrum of the product blue crystals differed from that of KI by having additional features at 9.1 and 11.1 eV. The XPS peaks centered at 9.0 and 11.1 eV that did not correspond to any other primary element peaks were assigned to  $H^-(n=1/4)E_b = 11.2$  eV hydride ion (Eq. (A.18)) in two different chemical environments. Furthermore, the reported minimum heats of formation of KHI by the catalytic reaction of potassium with atomic hydrogen and KI were over –2000 kJ/mol  $H_2$  compared to the enthalpy of combustion of hydrogen of –241.8 kJ/mol  $H_2$  [36]. The implications are that a new field of novel hydrogen chemistry has been discovered that represents a new source of energy with the potential for direct conversion of plasma to electricity [37,38].

## 5. Conclusion

Characteristic emission was observed from  $K^{3+}$  which confirmed the resonant nonradiative energy transfer of

3 · 27.2 eV from atomic hydrogen to atomic potassium (Eq. (A.5)). The predicted  $H^-(1/4)$  hydride ion of hydrogen catalysis by potassium catalyst given by Eqs. (A.5)–(A.7) and Eq. (A.18) was observed spectroscopically at 110 nm corresponding to its predicted binding energy of 11.2 eV.

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## Appendix A.

### A.1. Catalysts

The mechanism of EUV emission and formation of novel hydrides cannot be explained by the conventional chemistry of hydrogen; rather it must have been due to a novel chemical reaction between catalyst and atomic hydrogen. Mills [1–38] predicts that certain atoms or ions serve as catalysts to release energy from hydrogen to produce an increased binding energy hydrogen atom called a *hydrino atom* having a binding energy of

$$\text{Binding energy} = \frac{13.6 \text{ eV}}{n^2}, \quad (\text{A.1})$$

$$\text{where } n = \frac{1}{2}, \frac{1}{4}, \dots, \frac{1}{p} \quad (\text{A.2})$$

and  $p$  is an integer greater than 1, designated as  $H(\alpha_H/p)$  where  $\alpha_H$  is the radius of the hydrogen atom. Hydrinos are predicted to form by reacting an ordinary hydrogen atom with a catalyst having a net enthalpy of reaction of about

$$m \times 27.2 \text{ eV}, \quad (\text{A.3})$$

where  $m$  is an integer. This catalysis releases energy from the hydrogen atom with a commensurate decrease in size of the hydrogen atom,  $r_n = n\alpha_H$ . For example, the catalysis of  $H(n=1)$ – $H(n=1/2)$  releases 40.8 eV, and the hydrogen radius decreases from  $\alpha_H$  to  $\frac{1}{2}\alpha_H$ .

The excited energy states of atomic hydrogen are also given by Eq. (A.1) except that

$$n = 1, 2, 3, \dots \quad (\text{A.4})$$

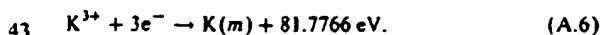
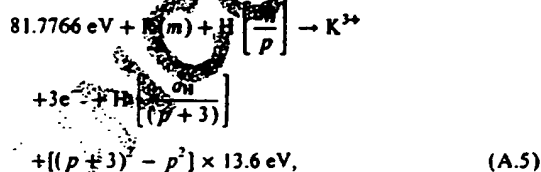
The  $n=1$  state is the “ground” state for “pure” photon transitions (the  $n=1$  state can absorb a photon and go to an excited electronic state, but it cannot release a photon and go to a lower-energy electronic state). However, an electron transition from the ground state to a lower-energy state is possible by a nonradiative energy transfer such as multipole coupling or a resonant collision mechanism. These lower-energy states have fractional quantum numbers,  $n = 1/\text{integer}$ . Processes that occur without photons and that

require collisions are common. For example, the exothermic chemical reaction of  $H + H$  to form  $H_2$  does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body,  $M$ , to remove the bond energy— $H + H + M \rightarrow H_2 + M^*$  [43]. The third body distributes the energy from the exothermic reaction, and the end result is the  $H_2$  molecule and an increase in the temperature of the system. Some commercial phosphors are based on non-radiative energy transfer involving multipole coupling. For example, the strong absorption strength of  $Sb^{3+}$  ions along with the efficient nonradiative transfer of excitation from  $Sb^{3+}$  to  $Mn^{2+}$ , are responsible for the strong manganese luminescence from phosphors containing these ions [44]. Similarly, the  $n = 1$  state of hydrogen and the  $n = 1/\text{integer}$  states of hydrogen are nonradiative, but a transition between two nonradiative states is possible via a nonradiative energy transfer, say  $n = 1-1/2$ . In these cases, during the transition the electron couples to another electron transition, electron transfer reaction, or inelastic scattering reaction which can absorb the exact amount of energy that must be removed from the hydrogen atom. Thus, a catalyst provides a net positive enthalpy of reaction of  $m \times 27.2$  eV (i.e. it absorbs  $m \times 27.2$  eV where  $m$  is an integer). Certain atoms or ions serve as catalysts which resonantly accept energy from hydrogen atoms and release the energy to the surroundings to effect electronic transitions to fractional quantum energy levels. Recent analysis of mobility and spectroscopy data of individual electrons in liquid helium show direct experimental evidence that electrons may have fractional principal quantum energy levels [35].

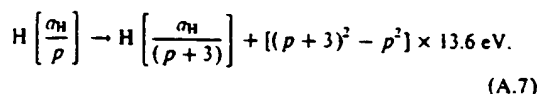
According to Mills [1–38], a catalytic system is provided by the ionization of  $t$  electrons from an atom or ion to a continuum energy level such that the sum of the ionization energies of the  $t$  electrons is approximately  $m \times 27.2$  eV where  $m$  is an integer.

#### A.2. Potassium

One such atomic catalytic system involves potassium atoms. The first, second, and third ionization energies of potassium are 4.34066, 31.63, and 81.776 eV, respectively [39]. The triple ionization ( $t = 3$ ) reaction of  $K-K^{3+}$ , then, has a net enthalpy of reaction of 81.776 eV, which is equivalent to  $m = 3$  in Eq. (A.3).



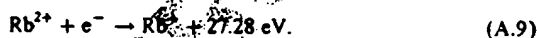
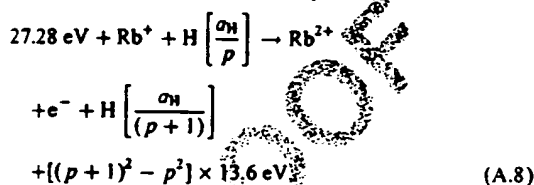
The overall reaction is



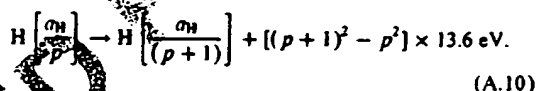
Vaporized atomic potassium was formed by hydrogen reduction and thermal decomposition of potassium carbonate.

#### A.3. Rubidium ion

Rubidium ions can also provide a net enthalpy of a multiple of that of the potential energy of the hydrogen atom. The second ionization energy of rubidium is 27.28 eV. The reaction  $Rb^+ - Rb^{2+}$  has a net enthalpy of reaction of 27.28 eV, which is equivalent to  $m = 1$  in Eq. (A.3).



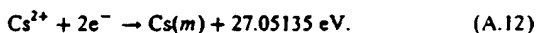
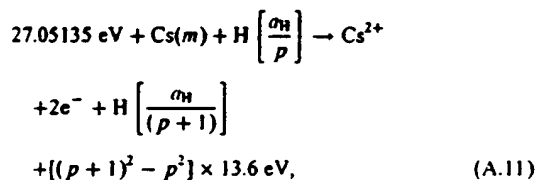
The overall reaction is



Rubidium metal may form  $RbH$  which may provide gas phase  $Rb^+$  ions, or rubidium metal may be ionized to provide gas phase  $Rb^+$  ions.  $Rb^+$  ion emission was observed in the EUV spectrum of rubidium metal.

#### A.4. Cesium

A catalytic system is provided by the ionization of two electrons from a cesium atom each to a continuum energy level such that the sum of the ionization energies of the two electrons is approximately 27.2 eV. The first and second ionization energies of cesium are 3.89390 and 23.15745 eV, respectively [39]. The double ionization ( $t = 2$ ) reaction of  $Cs-Cs^{2+}$ , then, has a net enthalpy of reaction of 27.05135 eV, which is equivalent to  $m = 1$  in Eq. (A.3).





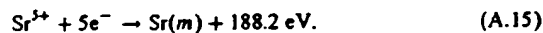
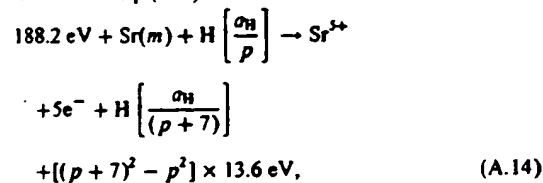
- 1 The overall reaction is

$$\text{H} \left[ \frac{a_0}{p} \right] \rightarrow \text{H} \left[ \frac{a_0}{(p+1)} \right] + [(p+1)^2 - p^2] \times 13.6 \text{ eV.} \quad (\text{A.13})$$

- 3 Vaporized atomic cesium was formed by hydrogen reduction and thermal decomposition of the carbonate.

#### A.5. Strontium

- 5 One such catalytic system involves strontium. The first through the fifth ionization energies of strontium are 5.69484, 11.03013, 42.89, 57, and 71.6 eV, respectively [39]. The ionization reaction of  $\text{Sr}-\text{Sr}^{5+}$ , ( $t=5$ ), then, has a net enthalpy of reaction of 188.2 eV, which is equivalent to  $m=7$  in Eq. (A.3).



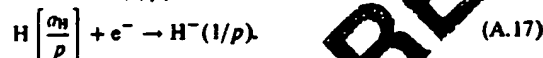
- 11 The overall reaction is

$$\text{H} \left[ \frac{a_0}{p} \right] \rightarrow \text{H} \left[ \frac{a_0}{(p+7)} \right] + [(p+7)^2 - p^2] \times 13.6 \text{ eV.} \quad (\text{A.16})$$

- 13 Vaporized atomic strontium was formed by heating the metal to 700°C.

#### A.6. Hydride ion

- 15 A novel hydride ion having extraordinary chemical properties given by Mills [1] is predicted to form by the reaction of an electron with a hydrino (Eq. (A.17)). The resulting hydride ion is referred to as a hydrino hydride ion, designated as  $\text{H}^-(1/p)$ .



- 21 The hydrino hydride ion is distinguished from an ordinary hydride ion having a binding energy of 0.8 eV. The hydrino hydride ion is predicted to comprise a hydrogen nucleus and two indistinguishable electrons at a binding energy according to the following formula:

$$\begin{aligned} \text{Binding energy} &= \frac{m_e \sqrt{s(s+1)}}{8\mu_0 a_0^3 [(1 + \sqrt{s(s+1)})/p]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \\ &\quad \left( 1 + \frac{2^2}{[(1 + \sqrt{s(s+1)})/p]^3} \right), \quad (\text{A.18}) \end{aligned}$$

- 25 where  $p$  is an integer greater than one,  $s=1/2$ ,  $\hbar$  is Planck's constant bar,  $\mu_0$  is the permeability of vacuum,  $m_e$  is the

mass of the electron,  $\mu_e$  is the reduced electron mass,  $a_0$  is the Bohr radius, and  $e$  is the elementary charge. The ionic radius is

$$r_1 = \frac{a_0}{p} (1 + \sqrt{s(s+1)}), \quad s = \frac{1}{2} \quad (\text{A.19})$$

From Eq. (A.19), the radius of the hydrino hydride ion  $\text{H}^-(1/p)$ ;  $p$  = integer is  $1/p$  that of ordinary hydride ion,  $\text{H}^-(1/1)$ . Compounds containing hydrino hydride ions have been isolated as products of the reaction of atomic hydrogen with atoms and ions identified as catalysts by EUV emission [5,7–34,36].

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